

the relative probabilities of any two states s_1 and s_2 doesn't change. Indeed, let's number all the states with integers in ~~classical~~ the order of increasing energy, so that now label s is an integer and $s+1$ and s label neighboring states. Then $s_2 = s_1 + k$ for some integer k . Then

$$\frac{p_{s_2}}{p_{s_1}} = \frac{p_{s_1+k}}{p_{s_1}} = \frac{p_{s_1+1}}{p_{s_1}} \frac{p_{s_1+2}}{p_{s_1+1}} \cdots \frac{p_{s_1+k}}{p_{s_1+k-1}} = \text{const} \text{ since each}$$

term in the product is const. Finally, because of the normalization condition the probabilities themselves must remain constant. Indeed, for any s_0

$$p_{s_0} = p_{s_0}/1 = \frac{p_{s_0}}{\sum_s p_s} = \frac{1}{\sum_s (p_s/p_{s_0})} = \text{const} \text{ since each term}$$

in the denominator is constant.

Great, so then only E_s in (*) changes and we have:

$$\begin{aligned} p &= - \left(\frac{\partial U}{\partial V} \right)_{E,N} = - \frac{\partial}{\partial V} \left(\sum_s E_s p_s \right) = - \sum_s \frac{\partial E_s}{\partial V} p_s = \\ &= - \sum_s \frac{\partial E_s}{\partial V} \frac{e^{-E_s/k}}{Z}, \quad \text{QED} \quad (5) \end{aligned}$$

$$(b) \quad (3.59) \Rightarrow E_s = \text{blah} \cdot L^{-2} = \text{blah} \cdot V^{-2/3}$$

$$\frac{\partial E_s}{\partial V} = -\frac{2}{3} \text{ blah } V^{-5/3} = -\frac{2}{3} \frac{E_s}{V}, \quad \text{QED} \quad (5)$$

$$(c) \quad p = - \sum_s -\frac{2}{3V} E_s \frac{e^{-E_s/k}}{Z} = \frac{2}{3V} \sum_s E_s p_s = \frac{2U}{3V}, \quad \text{QED} \quad (5)$$

(15)
(15)

③ Kittel 6.9

We will make use of formulas (6.47) – (6.50). We need to eva-